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(54) Title: VAPOR PHASE SILOXANE DRY CLEANING PROCESS

(57) Abstract: The process of the present invention is directed to a dry cleaning process, comprising the use of volatile cyclic, linear or branched siloxanes in the vapor phase for the cleaning of soiled or stained fabrics. The linear or branched siloxanes have the formula: $M_{2+y+2z}D_xT_yQ_z$ wherein: M is $R^1{}_3SiO_{1/2}$; D is $R^2R^3SiO_{2/2}$; T is $R^4SiO_{3/2}$; and Q is $SiO_{4/2}$. R^1, R^2, R^3 and R^4 are each independently a monovalent hydrocarbon radical having form one to forthy carbon stoms; and x and y are each integers, wherein $0 < x < 10$ and $0 < y < 10$.and $0 < z < 10$. While the cyclic siloxanes have the formula (1) wherein R^5, R^6,R^7 and R^8 are each independently a monovalent hydrocarbon group having from one to forty carbon atoms; and a and b are each integers wherein $0 < a < 10$ and $0 < b < 10$, provided that $3 < (a + b) < 10$.

SUMMARY OF THE INVENTION

The process of the present invention is directed to a cleaning process, comprising the use of a volatile cyclic, linear or branched siloxane in the vapor phase for the cleaning of articles.

Further, the present invention provides for a process for cleaning soiled articles of manufacture comprising:

a) contacting the soiled article of manufacture with a vapor phase silicone compound;

b) allowing the vapor phase silicone compound in contact with the soiled article of manufacture to condense to the liquid phase becoming thereby a condensed silicone liquid; and

c) draining the condensed silicone liquid away from the article of manufacture whereby the soiled article of manufacture is cleaned.

In another embodiment the present invention provides for a process for cleaning soiled garments comprising:

a) contacting the soiled garment with a vapor phase silicone compound;

b) allowing the vapor phase silicone compound in contact with the soiled garment to condense to the liquid phase becoming thereby a condensed silicone liquid; and

c) draining the condensed silicone liquid away from the garment whereby the soiled garment is cleaned.

and Q is $SiO_{4/2}$

R^1, R^2, R^3 and R^4 are each independently a monovalent hydrocarbon radical having from one to forty carbon atoms; and

x and y are each integers, wherein $0 \leq x \leq 10$ and $0 \leq y \leq 10$ and $0 \leq z \leq 10$.

Suitable monovalent hydrocarbon groups include linear hydrocarbon radicals, branched hydrocarbon radicals, monovalent alicyclic hydrocarbon radicals, monovalent and aromatic or fluoro containing hydrocarbon radicals. Preferred monovalent hydrocarbon radicals are monovalent alkyl radicals, monovalent aryl radicals and monovalent aralkyl radicals.

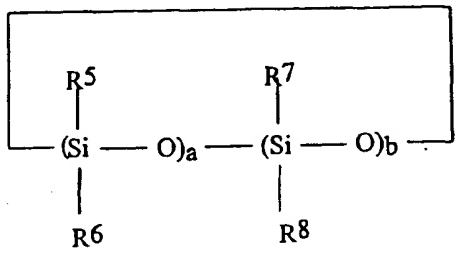
As used herein, the term "(C_1-C_6)alkyl" means a linear or branched alkyl group containing from 1 to 6 carbons per group, such as, for example, methyl, ethyl, propyl, iso-propyl, n-butyl, iso-butyl, sec-butyl, tert-butyl, pentyl, hexyl, preferably methyl.

As used herein, the term "aryl" means a monovalent unsaturated hydrocarbon ring system containing one or more aromatic or fluoro containing rings per group, which may optionally be substituted on the one or more aromatic or fluoro containing rings, preferably with one or more (C_1-C_6)alkyl groups and which, in the case of two or more rings, may be fused rings, including, for example, phenyl, 2,4,6-trimethylphenyl, 2-isopropylmethylphenyl, 1-pentalenyl, naphthyl, anthryl, preferably phenyl.

As used herein, the term "aralkyl" means an aryl derivative of an alkyl group, preferably a (C_2-C_6)alkyl group, wherein the alkyl portion of the aryl derivative may, optionally, be interrupted by an oxygen atom, such as, for example, phenylethyl, phenylpropyl, 2-(1-naphthyl)ethyl, preferably phenylpropyl, phenyoxypropyl, biphenyloxypropyl.

ranging from 0.01 to 760 mm Hg at a temperature ranging from about 10 °C to about 300 °C.

In another embodiment, the cyclic siloxane comprises one or more compounds of the structural formula (II):



(II)

wherein:

R^5, R^6, R^7 and R^8 are each independently a monovalent hydrocarbon group having from one to forty carbon atoms; and

a and b are each integers wherein $0 \leq a \leq 10$ and $0 \leq b \leq 10$, provided that $3 \leq (a + b) \leq 10$.

In yet another embodiment, the cyclic siloxane comprises one or more of, octamethylcyclotetrasiloxane, decamethylcyclopentasiloxane, dodecamethylcyclohexasiloxane, tetradecamethylcycloheptasiloxane. In a more highly preferred embodiment, the cyclic siloxane of the present invention comprises octamethylcyclotetrasiloxane or decamethylcyclopentasiloxane. In yet another embodiment, the cyclic siloxane component of the composition of the present invention consists essentially of decamethylcyclopentasiloxane.

Suitable cyclic siloxanes are made by known methods, such as, for example, hydrolysis and condensation of alkylhalosilanes, e.g. dimethyldichlorosilane, and are commercially available.

the process of the present invention is performed at a pressure that is varied among the steps of the process, e.g. initially contacting the garment to be cleaned with a vapor at a pressure below atmospheric followed by raising the pressure to atmospheric pressure to condense the vapor in the garment and allow the cleaning fluids to drain away from the garment.

Alternatively, the articles remain in the cleaning vessel and the silicone or silicone containing solvent is removed by various means and the articles are dried in the cleaning vessel as is commonly seen in typical dry cleaning machines.

An article, such as for example, a textile or leather article, typically, a garment, is cleaned by contacting the article with the vapors of the composition of the present invention. In a preferred embodiment, the articles to be cleaned include textiles made from natural fibers, such as for example, cotton, wool, linen and hemp, from synthetic fibers, such as, for example, polyester fibers, polyamide fibers, polypropylene fibers and elastomeric fibers, from blends of natural and synthetic fibers, from natural or synthetic leather or natural or synthetic fur.

The article and dry cleaning composition are then separated, by, for example, one or more of draining and centrifugation. In a preferred embodiment, separation of the article and dry cleaning composition is followed by the application of heat, preferably, heating to a temperature of from 15°C to 120°C, preferably from 20°C to 100°C, or reduced pressure, preferably, a pressure of from 1 mm Hg to 750 mm Hg, or by application of both heat and reduced pressure, to the article.

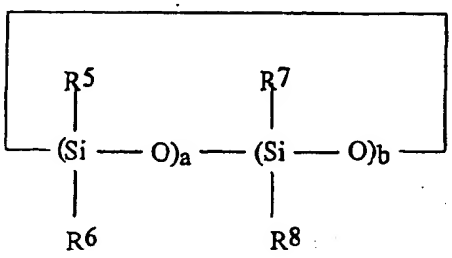
Testing for oil soluble stain removal was accomplished using a blue 50/50 cotton/poly cloth and a red satin fabric. The approximately 2 inch square samples were stained with motor oil, suspended by wires in a large

was reduced to 1-2 mm Hg and the temperature of the solvent reservoir was raised to 70-80 °C. The vapors were allowed to contact the stained fabrics for 5 minutes. After this time, the heat was removed, the vessel cooled and the samples removed and air dried and evaluated. All traces of the oil were removed from both fabrics. No extraction of the red dye from the satin fabric was observed.

Example 3 – Reduced Pressure, linear solvent

Samples of red satin and blue cotton/poly fabrics were treated with motor oil which was allowed to stain for 18 hours then attached to a wire holder and suspended above a reservoir of MD2M. The pressure in the system was reduced to 1-2 mm Hg and the temperature of the solvent reservoir was raised to 70-80 °C. The vapors were allowed to contact the stained fabrics for 5 minutes. After this time, the heat was removed, the vessel cooled and the samples removed and air dried and evaluated. All traces of the oil were removed from both fabrics. No extraction of the red dye from the satin fabric was observed.

3. The process of claim 1 wherein the silicone compound has the formula:



wherein:

R^5, R^6, R^7 and R^8 are each independently a monovalent hydrocarbon group having from one to forty carbon atoms; and

a and b are each integers wherein $0 \leq a \leq 10$ and $0 \leq b \leq 10$, provided that $3 \leq (a + b) \leq 10$.

4. The process of claim 2 wherein each of the steps a), b) and c) are independently conducted at a temperature ranging from about 10 °C to about 300 °C.

5. The process of claim 3 wherein each of the steps a), b) and c) are independently conducted at a temperature ranging from about 10 °C to about 300 °C.

6. The process of claim 4 wherein each of the steps a), b) and c) are independently conducted at a pressure ranging from about 0.01 mm Hg to about 760 mm Hg.

7. The process of claim 5 wherein each of the steps a), b) and c) are independently conducted at a pressure ranging from about 0.01 mm Hg to about 760 mm Hg.

12. The process of claim 11 wherein the silicone compound has the formula:

$$M_{2+y+2z}D_xT_yQ_z$$

wherein:

M is $R^1_3SiO_{1/2}$;

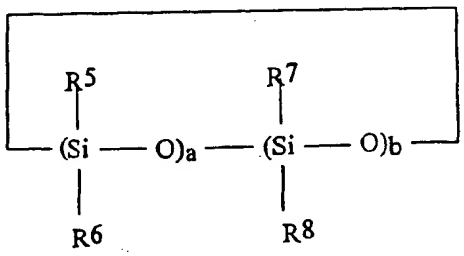
D is $R^2R^3SiO_{2/2}$;

T is $R^4SiO_{3/2}$;

and Q is $SiO_{4/2}$

R^1, R^2, R^3 and R^4 are each independently a monovalent hydrocarbon radical having from one to forty carbon atoms; and x and y are each integers, wherein $0 \leq x \leq 10$ and $0 \leq y \leq 10$ and $0 \leq z \leq 10$.

13. The process of claim 11 wherein the silicone compound has the formula:



wherein:

R^5, R^6, R^7 and R^8 are each independently a monovalent hydrocarbon group having from one to forty carbon atoms; and

a and b are each integers wherein $0 \leq a \leq 10$ and $0 \leq b \leq 10$, provided that $3 \leq (a + b) \leq 10$.

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A. CLASSIFICATION OF SUBJECT MATTER
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According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 D06L C11D D06F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DATABASE WPI Section Ch, Week 197826 Derwent Publications Ltd., London, GB; Class A26, AN 1978-46701A XP002206086 & JP 53 056203 A (LION FAT & OIL CO LTD), 22 May 1978 (1978-05-22) abstract	1,2,4,6, 8,10-12, 14,16,18
X	US 5 834 416 A (MORGAN DAVID LEE ET AL) 10 November 1998 (1998-11-10) column 6, line 44 - line 53 claims 1,2	10-12, 14,16,18
X	WO 99 10587 A (LAUBACH BERNADETTE STOREY ;MICELL TECHNOLOGIES (US); DEYOUNG JAMES) 4 March 1999 (1999-03-04) page 8, line 1 - line 32	1,10,11

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[X] Further documents are listed in the continuation of box C. [X] Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
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Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Richards, M

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nformation on patent family members

Ir tional Application No
I .,/US 02/04620

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
US 5676705	A	14-10-1997	AU	4942996 A	23-09-1996
			CA	2211412 A1	12-09-1996
			WO	9627704 A1	12-09-1996
			EP	0813628 A1	29-12-1997
			FI	973603 A	05-09-1997
			TR	9700901 T1	21-02-1998
			US	5683473 A	04-11-1997
			ZA	9601786 A	05-09-1997
US 2002004953	A1	17-01-2002	WO	0250366 A1	27-06-2002
US 4685930	A	11-08-1987	AU	585906 B2	29-06-1989
			AU	4981785 A	22-05-1986
			CA	1239326 A1	19-07-1988
			DE	3583377 D1	08-08-1991
			EP	0182583 A2	28-05-1986
			JP	1502875 C	28-06-1989
			JP	61119765 A	06-06-1986
			JP	63050463 B	07-10-1988
US 5942007	A	24-08-1999	US	5865852 A	02-02-1999
			AT	215631 T	15-04-2002
			AU	4993599 A	07-02-2000
			AU	5101799 A	07-02-2000
			BR	9912088 A	10-04-2001
			BR	9912811 A	02-05-2001
			CN	1309733 T	22-08-2001
			CN	1309734 T	22-08-2001
			DE	69901179 D1	08-05-2002
			DK	1084289 T3	24-06-2002
			EP	1084289 A1	21-03-2001
			EP	1092056 A1	18-04-2001
			HU	0102648 A2	28-12-2001
			NO	20010231 A	14-03-2001
			NO	20010232 A	14-03-2001
			PL	345504 A1	17-12-2001
			PL	345509 A1	17-12-2001
			TR	200100312 T2	23-07-2001
			TR	200100318 T2	21-08-2001
			WO	0004221 A1	27-01-2000
			WO	0004222 A1	27-01-2000
			US	6063135 A	16-05-2000
			US	6042617 A	28-03-2000
			US	6056789 A	02-05-2000
			US	6042618 A	28-03-2000
			US	6086635 A	11-07-2000
			US	6059845 A	09-05-2000

INTERNATIONAL SEARCH REPORT

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 685 930 A (KASPRZAK KENNETH A) 11 August 1987 (1987-08-11) cited in the application claims 1-9	1-19
A	US 5 942 007 A (BERNDT DIETER R ET AL) 24 August 1999 (1999-08-24) cited in the application claims 1-24	1-19

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